



Crystal Structures of 2-Phenyl-2*H*-1,2,3-Triazol-4-Carbaldehyde, an Active α -Glycosidase Inhibition Agent, and (1-Phenyl-1*H*-1,2,3-Triazol-4-yl)methyl Benzoate and (2-(4-Fluorophenyl)-2*H*-1,2,3-Triazole-4-yl)methanol, Two Moderately Active Compounds

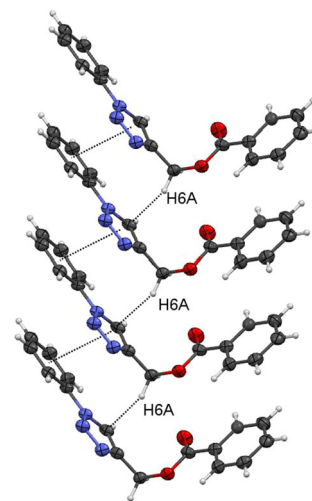
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Abstract The crystal structures of (1-phenyl-1*H*-1,2,3-triazol-4-yl)methyl benzoate, **1a**, (2-(4-fluorophenyl)-2*H*-1,2,3-triazole-4-yl)methanol, **2a**, and 2-phenyl-2*H*-1,2,3-triazol-4-carbaldehyde, **2b**, are reported. Compounds **1a** and **2a** were recently reported to exhibit mild α -glycosidase inhibition activity, while compound **2b** exhibited a much greater activity. Only small dihedral angles 6.52(4), 14.02(10) and 2.44(7)° are present between the triazolyl ring and the attached aryl rings in **1a**, **2a** and **2b**, respectively. The relatively flat compounds **2a** and **2b** contrast with compound **1a**, which is “V” shaped, with a dihedral angle between the near planar phenyltriazolyl-CH₂ and phenyl-CO₂CH₂ moieties of 88.11(4)°. The intermolecular interactions in **1a** are C–H...X (X = N or π (triazole) and π (triazole) ... π (phenyl): two different chains are formed, from (i) combinations of the C–H...N hydrogen bonds and (ii) combinations of the C–H... π and π ... π interactions. The intermolecular interactions in **2a** are C–H...O and C–F... π (phenyl): the C–H...O interactions generate a sheet of molecules, containing a network of rings. Classical O–H...O hydrogen bonds, and weaker C–H... π (triazolyl) and π (phenyl)... π (triazolyl)

interactions are present in **2b**: all three interactions together generate a chevron-type arrangement. Compound **1a** crystallizes in the *monoclinic* space group *P*2₁ with *a* = 4.5661(5), *b* = 10.5573(14), *c* = 13.9694(19) Å, β = 90.594(6)° and *Z* = 2. Compound **2a** crystallizes in the *monoclinic* space group *P*2₁ with *a* = 3.7175(7), *b* = 10.428(2), *c* = 10.689(3) Å, β = 90.521(6)° and *Z* = 2. Compound **2b** crystallizes in the *monoclinic* space group *P*2₁/*c* with *a* = 11.4130(5), *b* = 4.80280(10), *c* = 15.5916(11) Å, β = 103.373(7)° and *Z* = 4.

Graphical Abstract The relatively flat compounds, (2-(4-fluorophenyl)-2*H*-1,2,3-triazole-4-yl)methanol and 2-phenyl-2*H*-1,2,3-triazol-4-carbaldehyde, contrast with compound (1-phenyl-1*H*-1,2,3-triazol-4-yl)methyl benzoate, which is “V” shaped, with a dihedral angle between the near planar phenyltriazolyl-CH₂ and phenyl-CO₂CH₂ moieties of 88.11(4) o.



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Introduction

1,2,3-Triazole exists in two tautomeric forms, namely 1H-1,2,3-triazole and 2H-1,2,3-triazole, see Fig. 1. Derivatives of both forms have attracted much attention [1–3], in particular for their biological activities, which include as antiviral [4–6], antimalarial [7], antitubercular [8–10], antifungal [11, 12] anti-HIV [13], β -lactamase inhibition [14], anti-epileptic [15], anti-HSV [16], anti-inflammatory [17], antimicrobial [18, 19] and α -glycosidase inhibition agents [20–23]. Patents lodged in the period 2008–2011 for 1H-1,2,3-triazole and 2H-1,2,3-triazole derivatives have been included in a general survey for all triazolyl compounds [24].

A recent α -glycosidase inhibition study [23] involved a number of different 1-phenyl-1H- and 2-phenyl-2H-1,2,3-triazol derivatives. The crystal structures of three of the compounds from that study [20] have been determined, namely, (1-phenyl-1H-1,2,3-triazol-4-yl)methyl benzoate, **1a**, (2-(4-fluorophenyl)-2H-1,2,3-triazole-4-yl)methanol, **2a** and 2-phenyl-2H-1,2,3-triazole-4-carbaldehyde, **2b**, see Table 1. Compounds, **1a** and **2a**, exhibited little activity, while compound **2b**, exhibited a greater inhibition, as did all the 2-aryl-2H-1,2,3-triazole-4-carbaldehyde derivatives. It was suggested that the aldehydes act upon both yeast maltase and PPA, with the aldehyde groups reacting with amine groups in the enzyme polypeptide chain to form Schiff bases.

We now wish to report our structural findings.

Results and Discussion

The compounds were prepared as previously reported, see Scheme 1 [20].

Molecular Confirmations

Compounds **2a** and **2b** crystallize in the *monoclinic* space group, $P2_1$ with $Z = 2$, while compound **2b** crystallizes in the *monoclinic* space group, $P2_1/c$ with $Z = 4$. The

Fig. 1 **a** 1H-1,2,3-triazole, **b** 2H-1,2,3-triazole

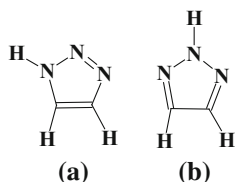


Table 1 Compounds mentioned in this article

| | |
|--|-------------------------------------------------------------------------------------------------------|
| | (1a : Ar = Ph, X = PhCO ₂ CH ₂ , Y = H) |
| | (1b : Ar = 4-MeC ₆ H ₄ , X = H, Y = F ₂ CH) |
| | (1c : Ar = 4-O ₂ NC ₆ H ₄ , X = Me, Y = MeCO) |
| | (1d : Ar = Ph, X = H, Y = pyridin-3-ylCO ₂ Me) |
| | (1e : Ar = 4-MeC ₆ H ₄ , X = H, Y = OCH |
| | (1f : Ar = 4-O ₂ NC ₆ H ₄ , X = OCH, Y = Me ₃ Si) |
| | (1g : Ar = 3-ClC ₆ H ₄ , X = H, Y = HOCH ₂) |
| | (1h : Ar = 3,5-Me ₂ C ₆ H ₃ , X = H, Y = HOCH ₂) |
| | (1i : Ar = 4-PhC ₆ H ₄ , X = H, Y = HOCH ₂) |
| | (1j : Ar = 4-HO ₂ CC ₆ H ₄ , X = H, Y = HOCH ₂) |
| | (1k : Ar = 2-HO ₂ CC ₆ H ₃ , X = H, Y = HOCH ₂) |
| | (1l : Ar = 2-HOC ₆ H ₄ , X = H, Y = HOCH ₂) |
| | (2b : Ar = 4-FC ₆ H ₄ , X = OCH, Y = H) |
| | (2a : Ar = Ph, X = HOCH ₂ , Y = H) |

asymmetric unit in each case consists of a single molecule, as illustrated in Fig. 2. Selected bond lengths and angles are listed in Table 2. The bond lengths and angles associated with the 1,2,3-triazole rings are in the regions normally found for 1-aryl-1H-1,2,3-triazoles [see for example 25–28] and for 2-aryl-2H-1,2,3-triazoles [see for example Refs. 28–33].

In each of **1a**, **2a** and **2b**, the triazolyl ring is essentially planar. The dihedral angles between the triazolyl and aryl rings are listed in Table 3.

A large range of dihedral angles have been reported for both 1-aryl-1H-1,2,3-triazole and 2-aryl-2H-1,2,3-triazole compounds, for example the angles are 0.34(17) and 87.1(2)°, respectively, in 4-difluoromethyl-1-(4-methylphenyl)-1H-1,2,3-triazole, **1b**, [34] and in one independent molecule of 1-[5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl]ethanone, **1c** [35], see Table 1. The carbon atoms of the methylene units in **2b** and **1a** are essentially coplanar with the attached triazolyl group. Compound **1a** has a “V” shape with the angle between the near planar phenyltriazolyl-CH₂ and phenyl-CO₂CH₂ moieties of 88.11(4)°.

Crystal Structures

Compound **1a**

The intermolecular interactions in **1a** are all weak, being C–H \cdots N hydrogen bonds, C–H \cdots π and π – π interactions. As illustrated in Fig. 3a, chains of molecules are propagated in the direction of the *b* axis, from combinations of C5–

Scheme 1 Reagents; *i* = D-glucose; *ii* = aq. CuSO₄; Δ , *iii* = NaIO₄; *iv* = NaBH₄, MeOH; *v* = HC \equiv C–CH₂OH, CuI; *vi* = PhCOCl

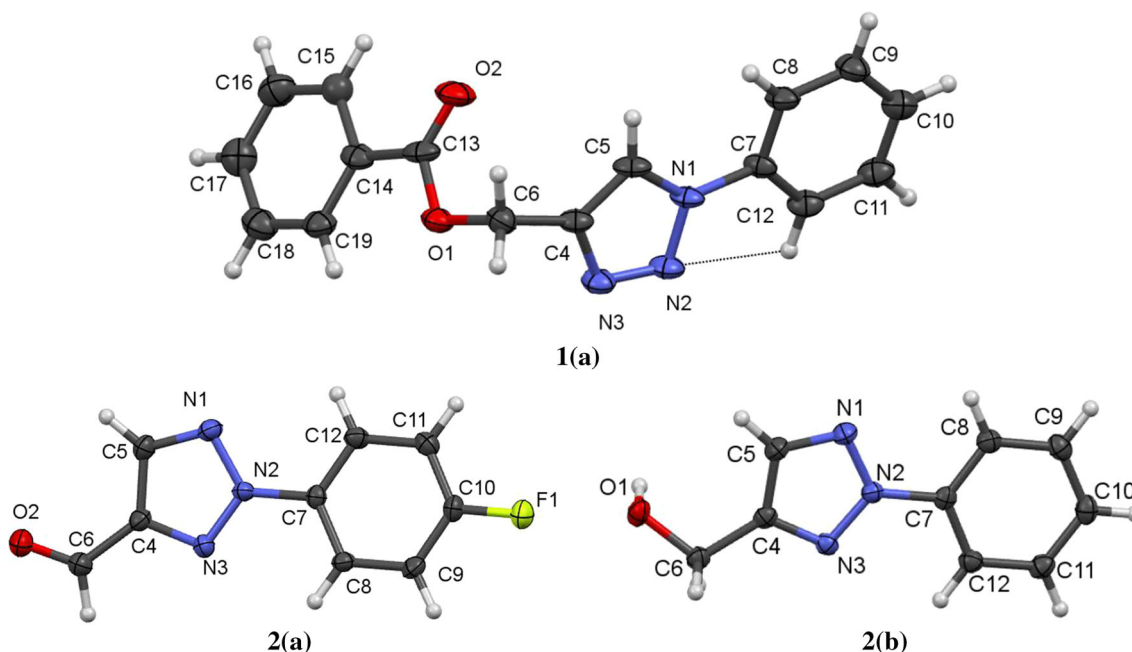
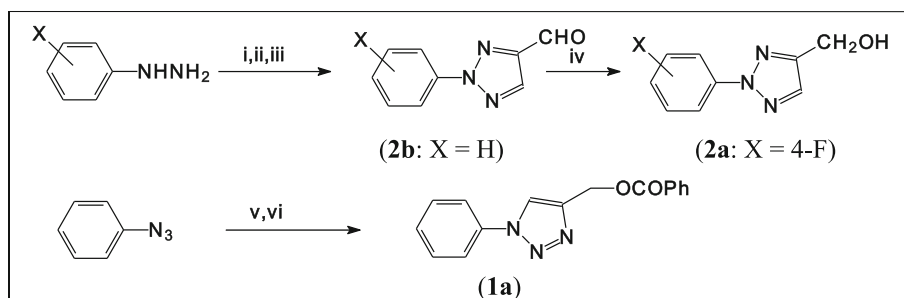


Fig. 2 Atom arrangements and the numbering schemes for **1a**, **2a** and **2b**. Probability ellipsoids are drawn at the 50 % level. The intramolecular hydrogen bond in **1a** is drawn as a thin dashed line

H5 \cdots N3, C5–H5 \cdots N2 and C8–H8 \cdots N3 hydrogen bonds, see Table 4 for the symmetry operations. Of these hydrogen bonds, the C5–H5 \cdots N3 is the most significant. With C5–H5 acting as donor to two acceptors, N2 and N3, $R_2^1(3)$ rings are generated. The C5–H5 \cdots N3, C5–H5 \cdots N2, and C8–H8 \cdots N3 hydrogen bonds individually generate C4, C4 and C6 chains of molecules.

Further, chain of molecules, this time propagated in the direction of the *a* axis, are formed from combinations of C6–H6A \cdots π (triazolyl) and π (phenyl) \cdots π (triazolyl) stacking interactions, see Fig. 3b; Table 4. This combination of interactions provides a chevron-type arrangement. The perpendicular distance between the best planes of combined triazolyl/ phenyl rings between layers is 3.359(3) Å, and with the Cg \cdots Cg separations of 3.738(3) Å, these $\pi\cdots\pi$ interactions are important. The packing of the molecules looking down the *b* axis is shown in Fig. 4.

The structure of a related compound, 1-phenyl-4-(pyridine-3-yl-CO₂CH₂)-1*H*-1,2,3-triazole (**1d**) [36] has been reported. There are some structural similarities between **1a** and **1d**: (i) the molecule of **1d** is also “V” shaped with the angle between the planar phenyltriazolyl CH₂ and phenyl-CO₂CH₂ moieties of 83.84°, (ii) the dihedral angle between the triazolyl and phenyl rings is 16.54 (11)°, and (iii) there are similar C–H \cdots π (triazole) and π (phenyl) \cdots π (triazolyl) interactions [Cg \cdots Cg = 3.895(1) Å]. However other intermolecular interactions are different in **1d**, being C–H \cdots N(py), C–H \cdots O(carbonyl) and C–H \cdots π (triazolyl) hydrogen bonds, which generate a different supramolecular array to that of **1a**.

Compound 2a

The intermolecular interactions in **2a** are C8–H8 \cdots O2 and C11–H11 \cdots O2 hydrogen bonds and C10–F1 \cdots π (phenyl)

Table 2 Selected geometric parameters, Å°

| | 1a | 2a | 2b |
|--------------|-----------|------------|------------|
| N1–N2 | 1.349(5) | 1.354(2) | 1.3356(12) |
| N2–N3 | 1.323(5) | 1.325(2) | 1.3410(12) |
| N3–C4 | 1.362(5) | 1.342(3) | 1.3358(13) |
| C4–C5 | 1.375(5) | 1.409(3) | 1.3999(15) |
| C5–N1 | 1.355(6) | 1.336(3) | 1.3309(15) |
| N1–N2–N3 | 106.8(3) | 115.38(16) | 115.28(9) |
| N2–N3–C4 | 109.4(4) | 104.10(16) | 103.69(8) |
| N3–C4–C5 | 108.0(4) | 108.35(18) | 108.25(9) |
| C4–C5–N1 | 104.8(4) | 108.91(18) | 109.43(10) |
| C5–N1–N2 | 110.9(4) | 103.26(17) | 103.34(9) |
| C5–N1–C7–C8 | 4.9(7) | | |
| N2–N1–C7–C12 | 7.6(6) | | |
| C5–N1–C7–C12 | 174.7(4) | | |
| N2–N1–C7–C8 | 172.8(4) | | |
| N1–N2–C7–C8 | | 164.27(19) | 0.70(15) |
| N1–N2–C7–C12 | | 14.9(3) | 179.39(15) |
| N3–N1–C7–C12 | | 168.6(2) | 3.04(14) |
| N3–N1–C7–C8 | | 12.3(3) | 176.87(9) |

Table 3 Interplanar angles, °

| Compound | Angle between triazole and phenyl rings° |
|-----------|------------------------------------------|
| 1a | 6.52(4) |
| 2a | 14.02(10) |
| 2b | 2.44(7) |

interactions. Table 4 lists the symmetry operations and geometric parameters. Combinations of the C8–H8...O2 and C11–H11...O2 hydrogen bonds generate sheets of molecules, composed of R_3^4 (24) rings, see Fig. 5a. The sheet undulates in the direction of the *b* axis, as shown in Fig. 4b. Both the C–H...O hydrogen bonds building the sheets are on the weak side. Stacks of molecules are generated from C10–F1... π (phenyl) interactions, see Fig. 5c. The Cg(phenyl)–Cg(triazolyl) distances in adjacent layers within the stacks are 4.2623(17) Å, which suggest any π (phenyl)– π (triazolyl) must be very weak. Figure 6 illustrates the packing of molecules of **2a**.

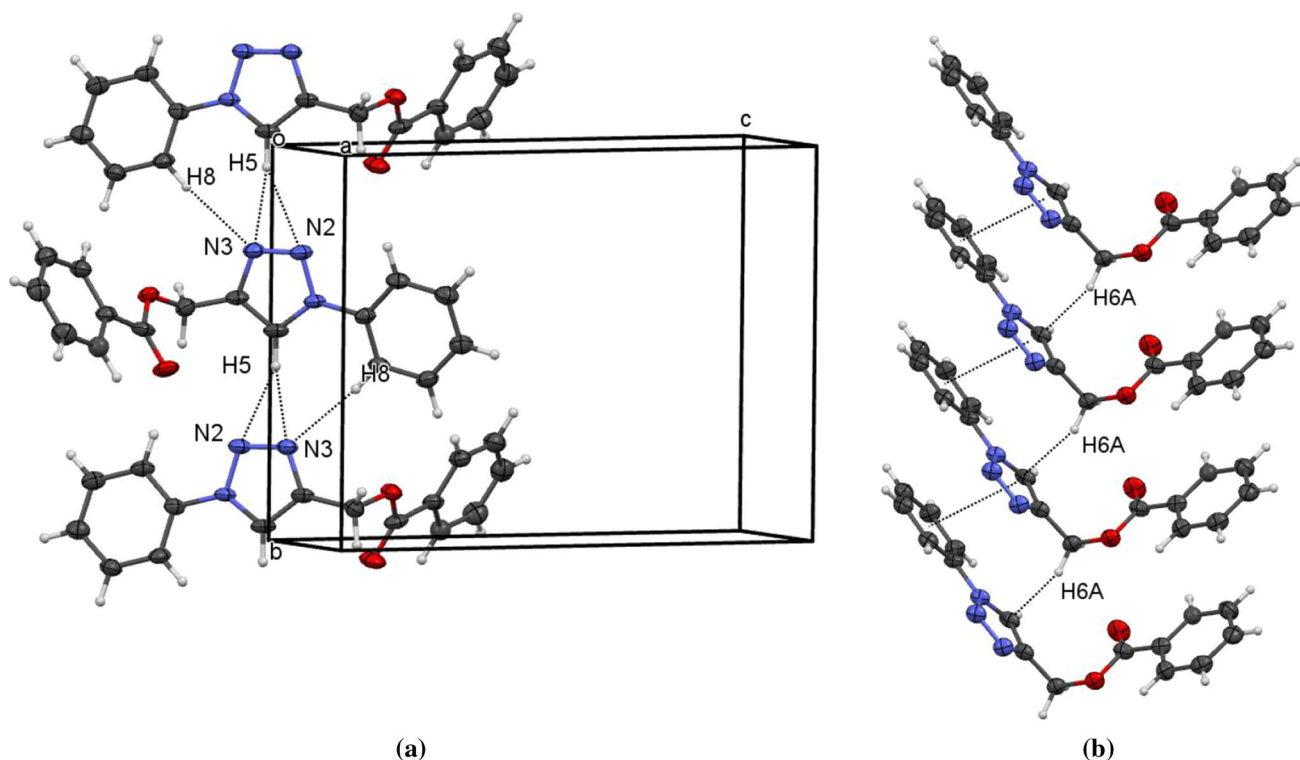


Fig. 3 Compound **1a**. **a** A chain of molecules generated in the direction of the *b* axis, from combinations of C5–H5...N3, C5–H5...N2 and C8–H8...N3 hydrogen bonds, **b** a further chain of molecules, propagated in the direction of the *a* axis, formed from C6–

H6A... π (triazole) and weak π (phenyl)... π (triazole) interactions. Table 4 lists the symmetry operations. Intermolecular interactions are drawn as *thin dashed lines*

Table 4 Geometric parameters (Å, °) for intra- and intermolecular interactions

| Compound | D–H...A | D–H | H...A | D...A | D–H...A | | |
|---------------------------------------|-----------------------------|------------|-------------------|------------|-----------|---------------------|---------------------|
| (a) Hydrogen bonds | | | | | | | |
| 1a | C12–H12...N2 | 0.95 | 2.48 | 2.799(6) | 100 | | |
| 1a | C5–H5...N2 ⁱ | 0.95 | 2.61 | 3.464(5) | 150 | | |
| 1a | C5–H5...N3 ⁱ | 0.95 | 2.31 | 3.239(5) | 165 | | |
| 1a | C8–H8...N3 ⁱ | 0.95 | 2.62 | 3.572(6) | 174 | | |
| 2a | C8–H8...O2 ⁱⁱ | 0.95 | 2.59 | 3.251(3) | 126 | | |
| 2a | C11–H11...O2 ⁱⁱⁱ | 0.95 | 2.61 | 3.373(3) | 138 | | |
| 2b | O1–H1...O1 ^{iv} | 0.84 | 1.89 | 2.7265(11) | 174 | | |
| | Y–X...Cg ^a | X...Cg | X _{perp} | γ | Y–X...Cg | Y...Cg | |
| (b) Y–X...π interactions ^a | | | | | | | |
| 1a | C6–H6A...Cg1 ⁱ | 2.62 | 2.614 | 1.91 | 143 | 3.456(5) | |
| 2a | C10–F1...Cg2 ⁱ | 3.7752(18) | 3.386 | 26.23 | 67.57(10) | 3.490(3) | |
| 2b | C6–C6B...Cg1 ⁱⁱ | 2.81 | 2.596 | 22.39 | 143 | 3.6500(11) | |
| | Cg(I)...Cg(J) | Cg...Cg | α | β | γ | CgI _{perp} | CgJ _{perp} |
| (c) π...π interactions ^a | | | | | | | |
| 1a | Cg1...Cg2 ⁱ | 3.738(3) | 6.54 | 22.39 | 28.00 | 3.301 | 3.456 |
| 1a | Cg2...Cg1 ⁱⁱ | 3.738(3) | 6.54 | 28.00 | 22.39 | 3.457 | 3.301 |
| 2a | Cg1...Cg2 ⁱⁱ | 4.2623(17) | 14.02 | 33.50 | 39.64 | 3.282 | 3.554 |
| 2a | Cg2...Cg1 ⁱ | 4.2624(17) | 14.02 | 39.64 | 33.50 | 3.554 | 3.282 |
| 2b | Cg1...Cg2 ⁱⁱⁱ | 3.7771(7) | 2.44 | 24.57 | 25.43 | 3.411 | 3.435 |
| 2b | Cg2...Cg1 ^{iv} | 3.7771(7) | 2.44 | 25.43 | 24.57 | 3.435 | 3.411 |

Symmetry operations for (a): *i* = 1 + *x*, *y*, *z*; *ii* = −1 + *x*, *y*, *z*; *iii* = *x*, 1 + *y*, *z*; *iv* = *x*, −1 + *y*, *z*

Symmetry codes for (b): *i* = −*x*, 1/2 + *y*, −*z*; *ii* = −*x*, 1/2 + *y*, 2−*z*; *iii* = 1 + *x*, *y*, −1 + *z*; *iv* = 1−*x*, −1/2 + *y*, 3/2−*z*

Symmetry codes for (c): *i* = 1 + *x*, *y*, *z*; *ii* = *x*, 1 + *y*, *z*

^a Cg1 and Cg2 are the centroids of the rings, containing atoms, N2 and C8, respectively; β is the angle between the vectors Cg...Cg and CgI_{perp} where CgI_{perp} is the perpendicular distance of CgI from the plane of ring J; γ is the angle between the vectors Cg...Cg and CgJ_{perp}

Compound 2b

Present in **2b** are classical O1–H1...O1 hydrogen bonds, and C6–H6B...π(triazolyl) and π(phenyl)...π(triazolyl) interactions. All three interactions together generate a chevron-type arrangement of molecules as illustrated in Fig. 7. The most significant of these interactions are O1–H1...O1 hydrogen bonds, which forms chains of molecules in the direction of the *b* axis. The packing of the molecules of **2b**, looking down the *b* axis is illustrated in Fig. 8. As in compound **2a**, none of the triazolyl nitrogen atoms are involved in any intermolecular interaction in **2b**.

Related Compounds

Comparisons of the structure of **2a** can be made with those reported for 1-(4-methylphenyl)-4-OCH-1*H*-1,2,3-triazole, **1e**, [37] and 1-(4-nitrophenyl)-4-trimethylsilyl-1*H*-1,2,3-triazol-5-carbaldehyde, **1f**, [38].

The structure of **1e**, which was only briefly discussed in the original article [37], exhibits significant differences with that of **2a**. Features of the structure of **1e** are (i) a near planar molecule, as shown by the dihedral angle of 7.1° between the triazolyl and the phenyl rings, (ii) C–H(phenyl)...O(=C) and C5–H5...N3 hydrogen bonds forming chains containing R₂² (10) rings propagated in the direction of the *a* axis, and relatively strong π(triazolyl)...π(triazolyl) and (iii) π(phenyl)...π(phenyl) interactions, in which the Cg...Cg distances and perpendicular distances between planes through the phenyltriazole fragments, in both cases are 3.865(4) and 3.436(4) Å, respectively.

The position of the aldehyde group on C5 of the triazole ring in **1f**, results in a much larger dihedral angle between the triazole and aryl planes of 62.34(5)°, compared to those in **2a** and **1e**. Again the carbonyl oxygen is involved in C–H...O hydrogen bonds, this time with a CH unit in the trimethylsilyl group: these C–H...O hydrogen bonds produce chains of molecules.

Fig. 4 Packing of molecules of **1a**, looking down the *b* axis

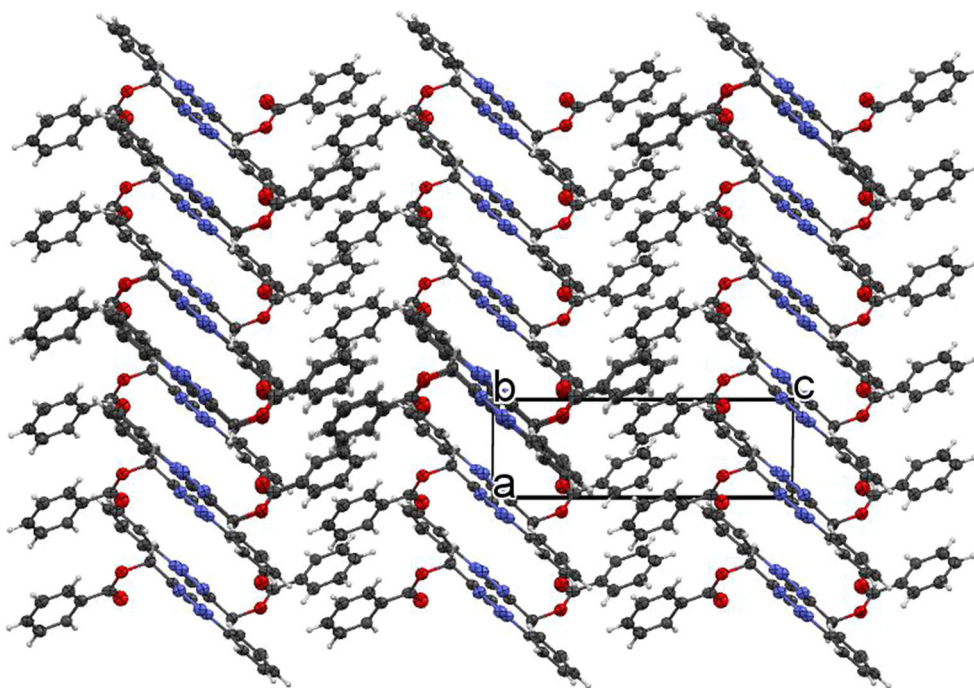
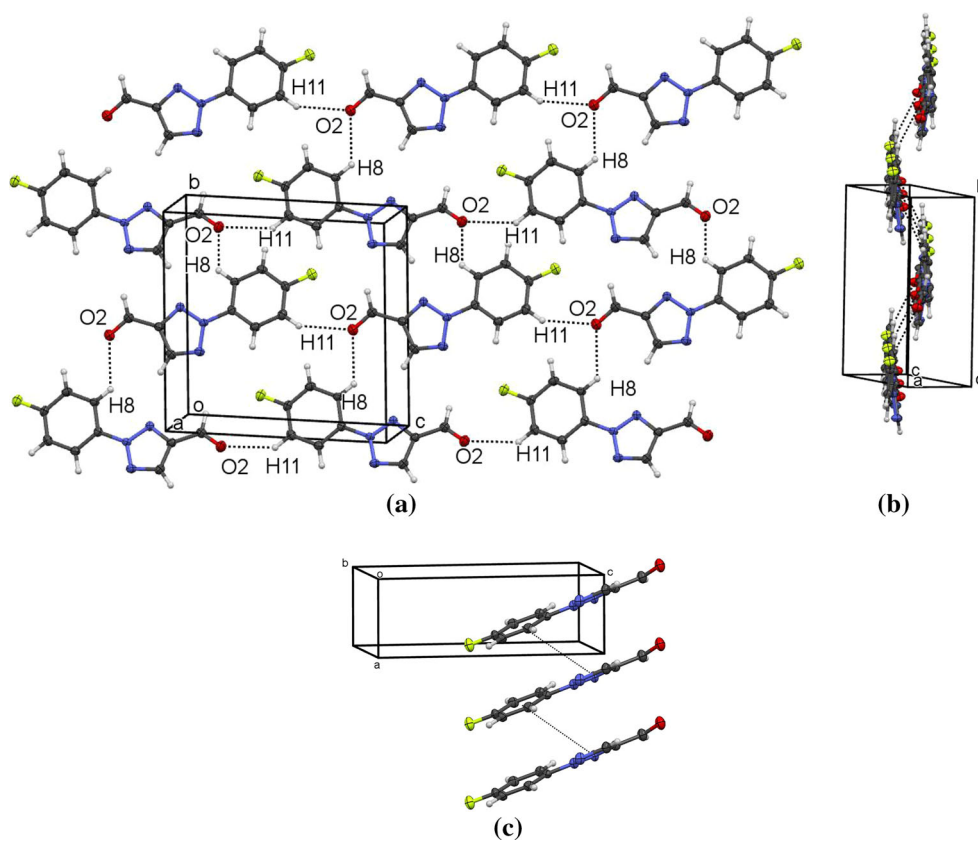


Fig. 5 Compound **2a**. **a** An undulating sheet of molecules of **2a**, formed from weak C11–H11...O2 and C8–H8...O2 hydrogen bonds, and composed of R_3^4 (24) rings, **b** an alternate view of the sheet shown in **a**, clearly indicating its undulating nature and its alignment along the *b* axis, **c** a stack of molecules, with π (phenyl)– π (triazole) stacking interactions, augmented by C10–F1... π (phenyl) interactions. Intermolecular interactions are drawn as thin dashed lines. Table 4 lists the symmetry operations



Comparison of the structure of **2a** can be made with the hemihydrate of 1-(3- C_6H_4)-4- $HOCH_2$ -1*H*-1,2,3-triazole, **1g**, [39], 1-(3,5-dimethylphenyl)-4- $HOCH_2$ -1*H*-1,2,3-

triazole, **1h**, [40] and 1-(4-biphenyl)-4- $HOCH_2$ -1*H*-1,2,3-triazole. **1i** [40] and 1-(4- $HO_2CC_6H_4$ -4- $HOCH_2$ -1*H*-1,2,3-triazole. **1j** [41], 1-(2- $HO_2CC_6H_4$ -4- $HOCH_2$ -1*H*-1,2,3-

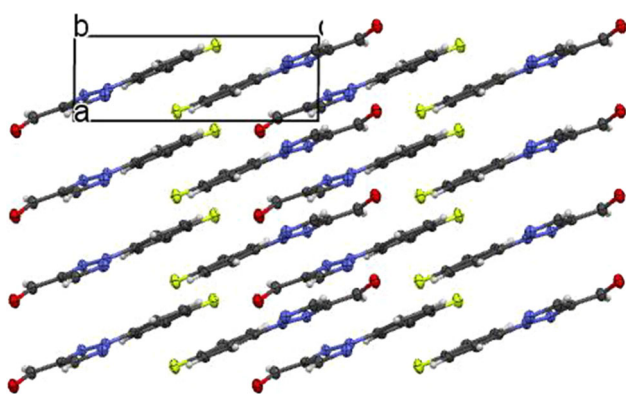


Fig. 6 Packing of molecules of **2a**, looking down the *b* axis

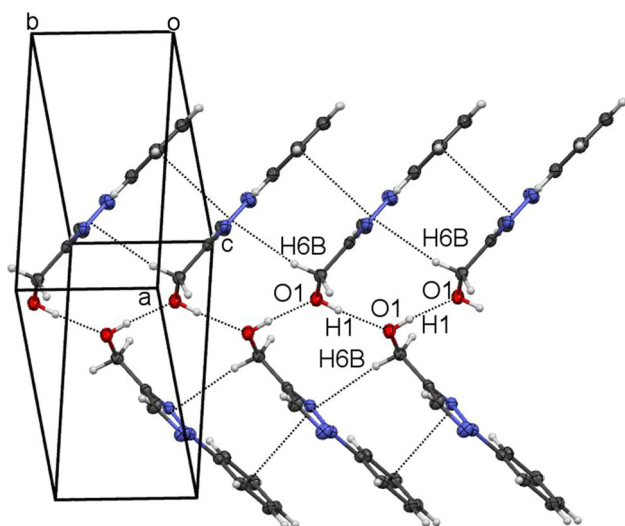


Fig. 7 Chevron type arrangement of molecules of **2b**, generated from strong classical O1–H1...O 1 intermolecular hydrogen bonds and weaker C6–H6B... π (triazole) and π (triazole)... π (phenyl) interactions. Table 4 lists the symmetry operations. Intermolecular interactions are drawn as thin dashed lines

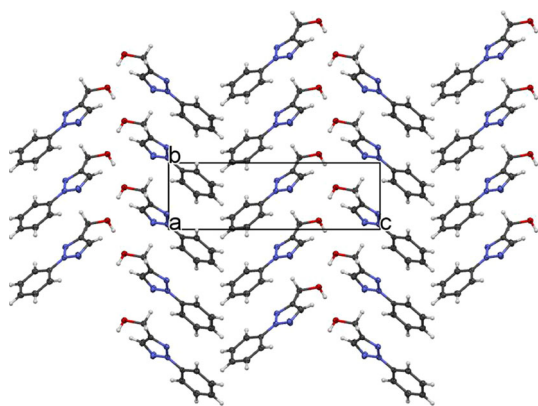


Fig. 8 Packing arrangement of molecules of **2b**, looking down the *b* axis

triazole. **1k** [41] and 1-(2-HOC₆H₄-4-HOCH₂-1*H*-1,2,3-triazole. **1l** [41].

In both 1-(4-biphenyl)-4-HOCH₂-1*H*-1,2,3-triazole, **1i**, and 1-(3,5-dimethylphenyl)-4-HOCH₂-1*H*-1,2,3-triazole, **1h**, [40], there are O–H...N3 hydrogen bonds involving the hydroxyl group. However in **1i**, these generate chains of molecules, while in **1h** centrosymmetric dimers, having R_2^2 (10) rings, are formed. The dihedral angles between the triazolyl and phenyl rings are 25.29(5) and 23.71(5)° in **1i** and **1h**, respectively, and thus are much larger than that in **2b** [2.44°] and must be a consequence of the crystal packing rather than any steric effect arising from the substituents. Neither **1i** nor **1h** exhibits π ... π stacking interactions.

In the hemihydrate of 1-(3-ClC₆H₄)-4-HOCH₂-1*H*-1,2,3-triazole, [**1g**.0.5(H₂O)] [39], the hydrate plays a significant role in the supramolecular array. The most important intermolecular interactions in [**1g**.0.5(H₂O)] are Ow–Hw...N3 and Ow–Hw...Ow hydrogen bonds, which generate chains of molecules of water and **1g** propagated in the direction of the *a*-axis. Additional features of the structure are O₆H₆ twelve-membered rings formed from O–H...O hydrogen bonds involving two hydrate molecules and the hydroxyl groups of two molecules each of the two independent molecules of **1g**. Also present in [(**1g**)₂(H₂O)] are weak π (phenyl)... π (phenyl) interactions.

As illustrated by [**1g**.0.5(H₂O)], the presence of additional donor centres radically changes the involvement of the triazole bound hydroxyl group. This is also very clearly illustrated by the group of compounds, **1j**–**1l** [26], in which the hydroxyl group on the triazole ring preferentially links with the hydroxyl or carboxylic acid substituents on the phenyl ring, leading to the formation of helices and other supramolecular architectures.

Conclusion

There appears to be no consistent intermolecular interaction, nor dihedral angle between the aryl and triazole rings, in either of the two series of aryl-1,2,3-triazoles. The dependence of the supramolecular array on the substituent(s) is clearly apparent.

Experimental

The compounds, **1a**, **2a** and **2b**, were prepared as reported [23]. For the structure determinations, crystals of **1a** were obtained from MeOH, **2a** from EtOH and **2b** from Me₂CO solutions.

Table 5 Crystal data and structure refinement

| | 2b | 1a | 1b |
|-----------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|
| Empirical formula | C ₉ H ₉ N ₃ O | C ₁₆ H ₁₃ N ₃ O ₂ | C ₉ H ₆ FN ₃ O |
| Formula weight | 175.19 | 279.29 | 191.17 |
| Temperature, K | 120(2) | 100(2) | 100(2) |
| Wavelength, Å | 0.71075 | 0.71075 | 0.71075 |
| Crystal system, space group | Monoclinic, <i>P</i> ₂ ₁ / <i>c</i> | Monoclinic, <i>P</i> ₂ ₁ | Monoclinic, <i>P</i> ₂ ₁ |
| Unit cell dimensions | | | |
| <i>a</i> , Å | 11.4130(5) | 4.5661(5) | 3.7175(7) |
| <i>b</i> , Å | 4.80280(10) | 10.5573(14) | 10.428(2) |
| <i>c</i> , Å | 15.5916(11) | 13.9694(19) | 10.689(3) |
| α , ° | 90 | 90 | 90 |
| β , ° | 103.373(7) | 90.594(6) | 90.521(6) |
| γ , ° | 90 | 90 | 90 |
| Volume, Å ³ | 831.47(7) | 673.37(15) | 414.35(16) |
| <i>Z</i> | 4 | 2 | 2 |
| Density (calculated) Mg/m ³ | 1.400 | 1.377 | 1.532 |
| Absorption coefficient, mm ^{−1} | 0.096 | 0.094 | 0.121 |
| <i>F</i> (000) | 368 | 292 | 196 |
| Crystal size, mm | 0.25 × 0.18 × 0.10 | 0.14 × 0.03 × 0.01 | 0.04 × 0.03 × 0.01 |
| Theta range for data collection, ° | 3.59–27.43 | 3.50–27.46 | 3.81–27.37 |
| Index ranges | −14 ≤ <i>h</i> ≤ 14; −5 ≤ <i>k</i> ≤ 6; −20 ≤ <i>l</i> ≤ 19 | −5 ≤ <i>h</i> ≤ 5; −13 ≤ <i>k</i> ≤ 13; −18 ≤ <i>l</i> ≤ 18 | −4 ≤ <i>h</i> ≤ 3; −13 ≤ <i>k</i> ≤ 13; −13 ≤ <i>l</i> ≤ 13 |
| Reflections collected | 8009 | 4663 | 5287 |
| Independent reflections | 1881 [R(int) = 0.0164] | 2762 [R(int) = 0.0664] | 1863 [R(int) = 0.0512] |
| Reflections observed (>2σ) | 1642 | 1884 | 1513 |
| Data completeness | 0.99 | 1.00 | 1.00 |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Refinement method | Full-matrix least-squares on <i>F</i> ² | Full-matrix least-squares on <i>F</i> ² | Full-matrix least-squares on <i>F</i> ² |
| Data/restraints/parameters | 1881/0/120 | 2762/1/190 | 1863/1/130 |
| Goodness-of-fit on <i>F</i> ² | 0.99 | 1.04 | 0.90 |
| Absolute structure parameter | – | 0.00 | 0.00 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> ₁ = 0.034 <i>wR</i> ₂ = 0.087 | <i>R</i> ₁ = 0.071 <i>wR</i> ₂ = 0.166 | <i>R</i> ₁ = 0.040 <i>wR</i> ₂ = 0.089 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.039 <i>wR</i> ₂ = 0.091 | <i>R</i> ₁ = 0.109 <i>wR</i> ₂ = 0.196 | <i>R</i> ₁ = 0.054 <i>wR</i> ₂ = 0.097 |
| Largest diff. peak and hole, e Å ^{−3} | 0.24 and −0.24 | 0.34 and −0.34 | 0.18 and −0.19 |
| CCDC No | 1,417,606 | 1,417,783 | 1,417,607 |

X-Ray Crystallography

Data for compounds **1a** and **2b** were obtained at 120(2) K while data for compound **2a** were collected at 100(2) K, all with Mo-K α radiation by means of a Bruker–Nonius Roper CCD camera on kappa-goniostat instrument of the NCS crystallographic service, based at the University of Southampton. Data collection, data reduction and unit cell refinement were achieved with DENZO [41] and

COLLECT [42] programs. Correction for absorption was achieved in each program SADABS 2007/2 [43]. The program MERCURY [44] was used in the preparation of the Figures. SHELXL97 [45] and PLATON [46] were used in the calculation of molecular geometry. The structures were solved by direct methods using SHELXS-97 [45] and fully refined by means of the program SHELXL-97 [45]. Difference map provided position for the aldehydic hydrogen atoms of **2b**. All other hydrogen atoms were

placed in calculated positions. Crystal data and structure refinement details are listed in Table 5.

Supplementary Material

Full details of the crystal structure determinations in cif format are available in the online version, at doi: (to be inserted), and have also been deposited with the Cambridge Crystallographic Data Centre with deposition numbers, 1417606, 1417783 and 1417607, respectively for **1a**, **2a** and **2b**. Copies of these can be obtained free of charge on written application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033); on request by e-mail to deposit@ccdc.cam.ac.uk or by access to <http://www.ccdc.cam.ac.uk>.

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